REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
25-06-2013	Performance/Technical Report (Monthly)	5/25/13 - 6/25/13

4. TITLE AND SUBTITLE
Polyfibroblast: A Self-Healing and Galvanic Protection Additive

5a. CONTRACT NUMBER

5b. GRANT NUMBER
N00014-09-1-0383

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Benkoski, Jason J.

5d. PROJECT NUMBER

5e. TASK NUMBER
FGY25

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
The Johns Hopkins University Applied Physics Laboratory
11100 Johns Hopkins Rd
Laurel, MD 20723

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
875 North Randolph Street
Arlington, VA 22203-1995

10. SPONSOR/MONITOR'S ACRONYM(S)
ONR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release: distribution is Unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.

15. SUBJECT TERMS
corrosion protection, self-healing, coatings, polymers

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
			UU		Jason J Benkoski
					19b. TELEPHONE NUMBER *(Include area code)*
U	U	U		5	240-228-5140

REDD-2013-232

POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #1

Prepared for:

Cody M. Reese
Logistics S&T Thrust Manager
Office of Naval Research
Code 30, Room 1149
875 North Randolph Street
Arlington, VA 22203-1995

Prepared by:

Jason J. Benkoski, Ph.D., Senior Research Scientist
The Johns Hopkins University Applied Physics Laboratory
The Milton S. Eisenhower Research Center
11100 Johns Hopkins Rd, MS 21-N109
Laurel, MD 20723
Tel. (240) 228-5140

Reporting Period: May 25 through June 25, 2013
Date of Report: June 25, 2013

TABLE OF CONTENTS

1 Summary

Using fourier-transform infrared spectroscopy, we monitored the hydrolytic degradation of OTS encapsulated within a polyurea shell. The degradation was so slow over the course of one month that it was easier to monitor IPDI degradation instead. We found first order reaction kinetics with an activation energy of roughly 46 kJ/mol.

2 Project Goals and Objectives

The four milestones for phase IV are as follows:

1. Develop on site inspection method for monitoring self-healing and coating health by month 3.
2. Develop a method for continuous monitoring of OTS degradation by month 5.
3. Demonstrate a method for measuring the fraction of broken microcapsules as a function of shear stress by month 6.
4. Establish baseline metrics for qualifying batches of microcapsules from the manufacturing process by month 12.

3 Key Accomplishments

3.1 Quantification of Microcapsule Composition

Up to this point in this program, the microcapsule composition was only quantified in terms of the fraction of liquid and solid. Acquired using thermogravimetric analysis (TGA), the measurements were performed sparingly. The consensus was that the 65% OTS microcapsules were approximately 35% polymer by weight and 65% OTS, as expected. The measurements seemingly indicated that the IPDI was completely consumed by the interfacial polymerization with water, PEI, and DETA.

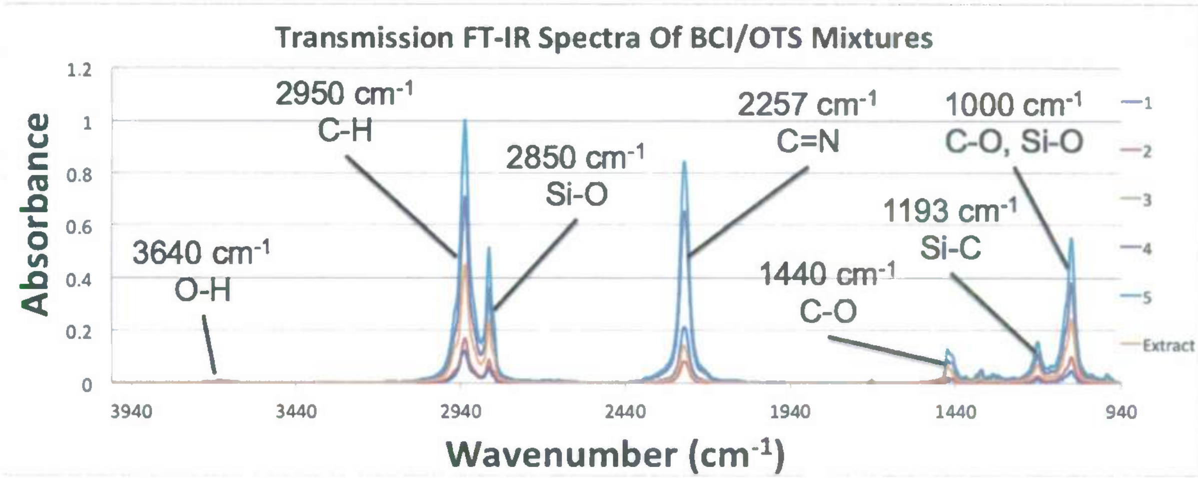

Figure 1. FTIR spectrum for 65% OTS microcapsule with major absorption peaks identified.

Fourier-transform infrared spectroscopy measures the infrared absorption peaks caused by thermal vibrations to accurately identify the presence of various organic functional groups. One can use Beer's Law to quantify the concentration of each chemical species by calibrating the height of the absorption peak with the molar concentration. Figure 1 shows that the 1193 cm^{-1} peak can be assigned to OTS, while the 2257 cm^{-1} peak can be assigned to IPDI.

Figure 2. Average of six FTIR measurements showing the weight percent of OTS and IPDI.

This technique yielded an average OTS concentration of 61% with a standard deviation of 1.5%, and an IPDI concentration of 1.3% with a standard deviation of 0.077%. The technique is used routinely to compare every sample with the expected baseline values.

3.2 OTS Hydrolysis

100 mg aliquots of 65% OTS microcapsules were placed in water and heated to a fixed temperature for extended periods of time to measure the temperature dependence of hydrolysis. Five temperatures were used in all: 30, 35, 40, 45, and 50°C. The OTS and IPDI concentrations were measured at each temperature periodically to record the amount of hydrolytic degradation using FTIR. The OTS concentration did not decrease appreciably over time. We therefore monitored the degradation of IPDI instead. Due to its greater reactivity, the IPDI likely scavenges water and protects the OTS before being consumed.

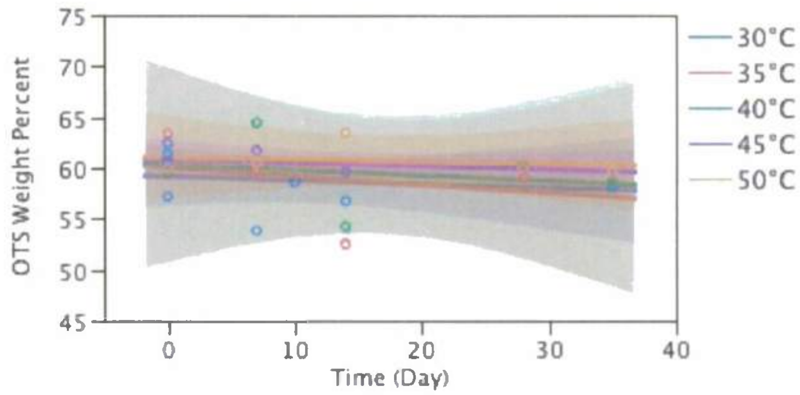

Figure 3. OTS concentration plotted versus time and grouped by temperature.

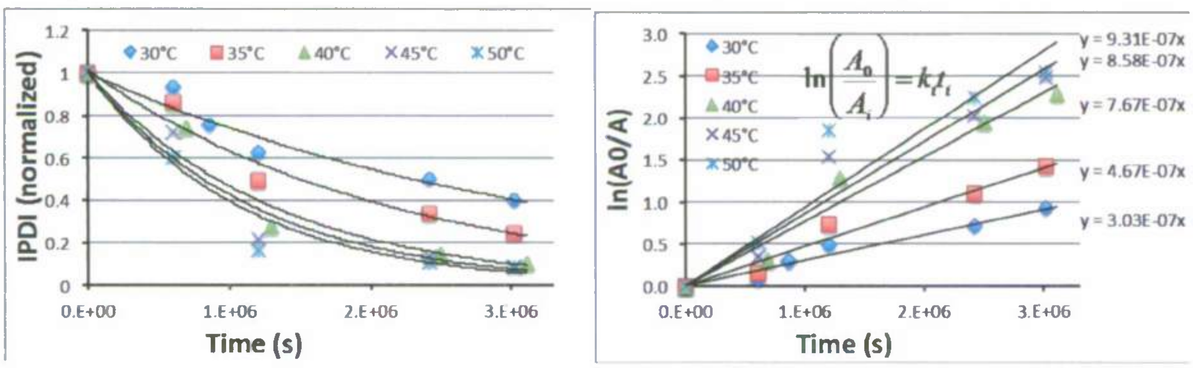

Figure 4. (left) IPDI concentration normalized versus OTS concentration and plotted versus time and grouped by temperature. (right) The log of the initial concentration divided by the final concentration is plotted on the right. The slopes of the linear fits correspond to the 1st order reaction rate constant.

The first order reaction rate constant (k) can be calculated by plotting the natural log of the initial concentration (A_0) divided by the final concentration (A_i) versus time (t). By doing so at each temperature, one can generate an Arrhenius plot to determine the activation energy of the reaction (E_a). Shown in Figure 5, we see that the activation energy comes out to 47 kJ/mol.

Since IPDI reacts much more quickly with water at these temperatures than what is measured here, the hydrolysis must be diffusion rate limited due to the microcapsule shell. This activation energy therefore corresponds to the temperature dependence of water diffusion through the shell. Note that the polyurea shell in this case contains silica inclusions.

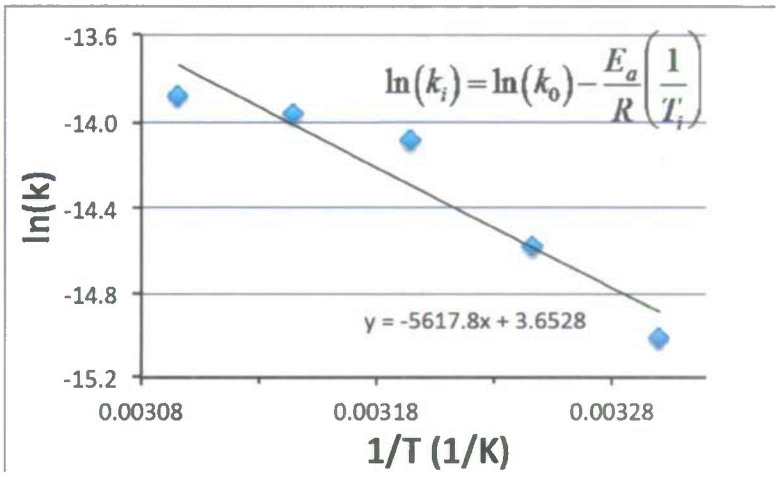

Figure 5. Arrhenius plot for the hydrolysis of IPDI.

Knowing the activation energy allows us to calculate the expected degradation rate at different temperatures and relative humidities. For example, one can compare the expected rate of degradation at 40°C and 100% relative humidity versus 25°C and 50% relative humidity. The hydrolysis would be roughly 7x faster at the higher temperature, meaning that samples soaked in water for 1 month at 40°C is equivalent to 7 months at ambient conditions.

3.3 Next Steps

Since it is the first milestone, the next immediate step is to develop an in situ test method for monitoring self-healing and the health of the coating in service. We propose the use of a handheld fluorescence microscope to image the tracer dye that is placed within all microcapsules. The fluorescence signal should facilitate the identification of OTS liquid, whether it remains within intact microcapsules, or whether it has flowed across the scratches.